

# Effect of Pressure on the Viscosity of Polymer Melts Swollen with Dissolved Carbon Dioxide.

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Viscosity is measured as a function of composition and pressure for polystyrene and PMMA melts containing 0-5 wt% carbon dioxide at 180 C. Viscosity is found to vary with the exponential of pressure multiplied by a coefficient  $b$ , which is of magnitude  $10^{-4}$  psi<sup>-1</sup> for both systems. However,  $b$  increases sharply with CO<sub>2</sub> content for the PS-CO<sub>2</sub> system, whereas it remains nearly constant for PMMA-CO<sub>2</sub>. Carbon dioxide also exhibits a stronger viscosity reduction effect in PS-CO<sub>2</sub> mixtures than in PMMA-CO<sub>2</sub>.

## INTRODUCTION

Dissolved carbon dioxide and other supercritical gases can greatly reduce the viscosity of molten polymers [1,2], leading to many promising applications of supercritical fluids in polymer processing. However, considerable pressure (~10 Mpa) is required to achieve significant solubility of carbon dioxide in polymer melts at typical processing temperatures. Thus the effect of pressure on the viscosity of polymer-carbon dioxide mixtures plays an important role in the rheological behavior of these systems. Here, the viscosities of polystyrene (PS) and polymethylmethacrylate (PMMA) melts containing up to 5 wt% dissolved carbon dioxide are measured as functions of pressure in a sealed, high-pressure capillary rheometer. The effect of pressure on viscosity is examined as a function of carbon dioxide content for both polymer melts to determine the viscoelastic scaling factor  $a_p$  due to pressure (see [2]). Finally, the experimentally determined  $a_p$  are used to isolate the effect of carbon dioxide content on viscosity, as represented by the compositional scaling factor  $a_c$  (see [2]).

## I - MATERIALS AND METHODS

Polydisperse, commercial grades of PS and PMMA, with molecular weights of approximately  $10^5$  are employed in the experiments. The PS material is supplied as 0.3 cm pellets, and the PMMA is supplied as a solid 1 cm diameter rod. The solid polymer materials are placed in a pressure vessel and soaked in carbon dioxide at room temperature and approximately 850 psi for about a week. The soaked polymer samples are then unloaded from the pressure vessel and placed on the pan of an electronic balance, where they are allowed to degas until a specified carbon dioxide content is reached. The CO<sub>2</sub>-impregnated polymer samples are then sealed in the barrel of the high-pressure capillary rheometer, and brought to the temperature and pressure required for the viscosity measurement. The geometries of the polymer sample (pellets for PS and solid rods for PMMA) are selected so that diffusion of carbon dioxide occurs on a slow enough time scale to allow loading of the sample in the rheometer without significant loss of carbon dioxide.

The high pressure capillary rheometer consists of a standard Instron capillary rheometer, mounted in the load frame of an Instron machine, with a specially constructed chamber mounted at the outflow end of the capillary to maintain backpressure on the sample and prevent foaming. The rheometer is a modified version of the rheometer developed by Gerhardt, et al. [3]. In the modified rheometer used here, backpressure is maintained by controlling the pressure of hydraulic oil, which fills the backpressure chamber. The pressure differential created by flow through the capillary is measured by means of a pressure transducer mounted upstream of the capillary, in the rheometer reservoir, and a pressure transducer mounted downstream of the capillary, in the backpressure chamber.

After the polymer sample is loaded in the rheometer, as described above, the rheometer temperature control system is activated to bring the rheometer and sample up to 180 °C, the temperature of the viscosity measurements. As the polymer begins to melt, the rheometer piston is moved to equilibrate the pressure of the sample with the pressure of the backpressure chamber. When the desired temperature and pressure are achieved, the rheometer piston is set in motion at constant speed to displace the sample at constant volumetric flow rate through the capillary. Both the upstream and downstream pressures are recorded, and the difference between these pressures, together with the capillary geometry and volumetric flow rate, are used to calculate the apparent viscosity of the sample and the apparent shear rate.

Apparent viscosity and apparent shear rates are corrected to obtain the true viscosities and shear rates by applying the Schummer correction, as described in [4]. Next, the effect of pressure on the viscosity of polymer melt samples containing CO<sub>2</sub> is determined by performing viscosity measurements at fixed shear rate, and varying the backpressure held on the sample. The average pressure P\* is determined from the upstream and downstream pressures by the method developed by Kwag, et al. [2]. The variation of viscosity,  $\eta$ , with P\* is fitted to an exponential form:

$$\eta(P^*) = \eta(P_o) \exp \{b(P^* - P_o)\} \quad (1)$$

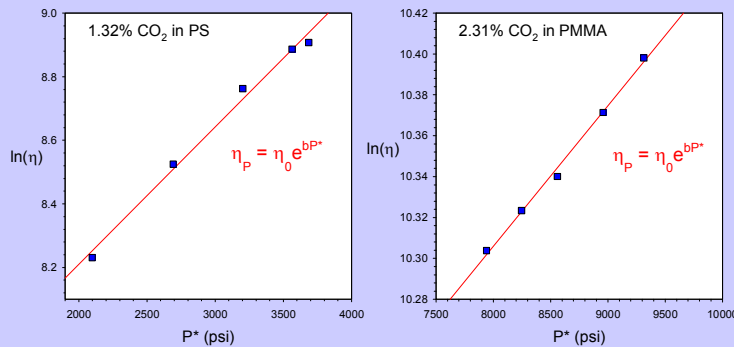
where b is the coefficient of pressure dependence, and P<sub>o</sub> is atmospheric pressure.

Using the viscoelastic scaling method developed by Kwag, et al. [2], the overall scaling factor  $a = a_p \cdot a_c$  is determined by shifting the viscosity curve (viscosity vs shear rate) for the polymer-CO<sub>2</sub> mixture onto the viscosity curve for the pure polymer melt to form a master curve. The pressure scaling factor is then calculated from the measured value for b, allowing the effect of carbon dioxide composition on viscosity to be isolated through calculation of a<sub>c</sub>.

## II – RESULTS

Examples of the variation of viscosity with pressure for PS and PMMA melts containing carbon dioxide are shown below, in Fig. 1. The data for both polymers are fitted very well by the exponential expression given in Eq. 1.

Figure 1: Variation of  $\eta$  with Pressure

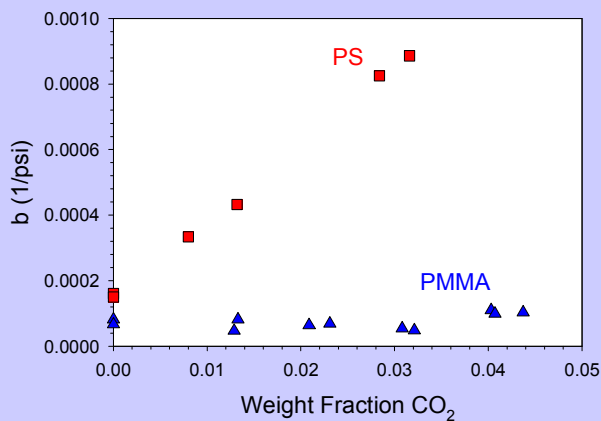


Estimation of characteristic pressure  $P^*$  where local  $dP/dz = \Delta P/L$ :

$$P^* = \frac{1}{b} \ln \left( \frac{b(P_1 - P_2)}{e^{-bP_2} - e^{-bP_1}} \right)$$

The  $b$  values for PS-CO<sub>2</sub> mixtures and PMMA-CO<sub>2</sub> mixtures are shown in Fig. 2.

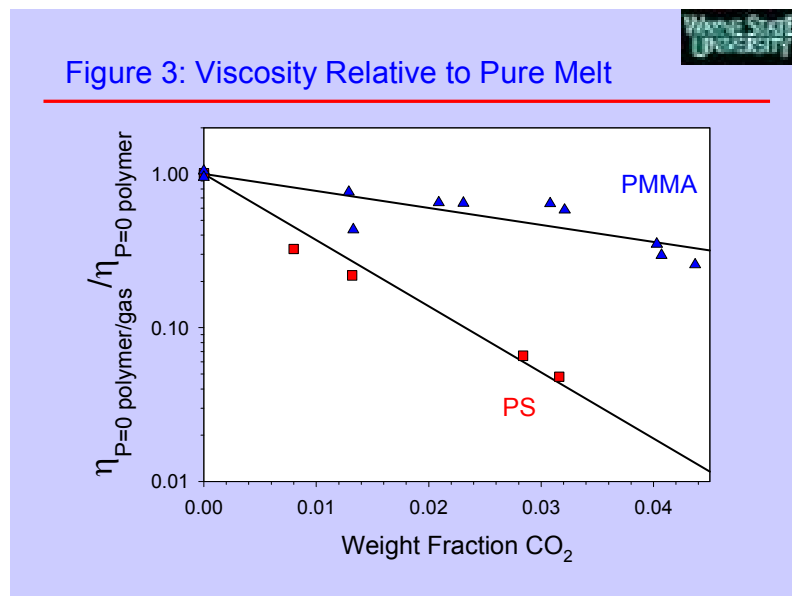
Figure 2: Coefficient of Pressure Dependence



Note that the pressure coefficient of viscosity  $b$  increases significantly with CO<sub>2</sub> content for polystyrene, while it remains essentially constant with CO<sub>2</sub> content for PMMA. This is a very important difference in the behavior of these two systems. Since PS and PMMA have very similar glass transition temperatures, near 100 °C, this difference cannot be attributed to an intrinsic difference in  $T_g$  of the pure melts. Free volume theories of polymer melt viscosity ascribe that the increase of viscosity with pressure is due to reduction in free volume upon compression, suggesting that the increase of  $b$  with CO<sub>2</sub> content in the case of PS-CO<sub>2</sub> mixtures may be due to an corresponding increase of compressibility. The absence of such an increase in  $b$  in the PMMA-CO<sub>2</sub> system, in turn, suggests that compressibility remains constant.

There are also striking differences in the variation of the viscoelastic scaling coefficient  $a_c$  for these two systems. Figure 3 shows that  $a_c$  varies more sharply with CO<sub>2</sub> content for the PS-CO<sub>2</sub> system than for the PMMA-CO<sub>2</sub> system. This means that the viscosity reduction that can

be achieved with a given amount of carbon dioxide is substantially greater in PS melts than in PMMA melts. As discussed above, this effect cannot be attributed to a difference in glass transition temperatures, which are similar for the two polymers.



Note that the viscoelastic scaling factor  $a_c$  is identical to the viscosity ratio plotted on the vertical axis in Fig. 3.

## CONCLUSION

The dependence of viscosity on pressure follows the exponential dependence of Eq. 1 for both PS-CO<sub>2</sub> mixtures and PMMA-CO<sub>2</sub> mixtures. Both systems exhibit coefficients  $b$  of magnitude  $10^{-4} \text{ psi}^{-1}$ , indicating that the effect of pressure on viscosity is important for pressures of about 1000 psi, and higher. However, the  $b$  values for the PS-CO<sub>2</sub> system increase strongly with CO<sub>2</sub> content, whereas the  $b$  values for the PMMA-CO<sub>2</sub> system remain nearly constant. Important differences are also observed in the ability of carbon dioxide to reduce melt viscosity in the two systems. Much greater viscosity reduction due to the swelling of the melt with CO<sub>2</sub> is seen in the PS-CO<sub>2</sub> system than in the PMMA-CO<sub>2</sub> system.

## REFERENCES :

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